

Effect of short-range order on the electronic structure and optical properties of the CuZn alloy : an augmented space approach.

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(Dated: February 6, 2008)

In this work we have combined the generalized augmented space method introduced by one of us with the recursion method of Haydock *et.al.* (GASR), within the framework of the local density functional based linear muffin-tin orbitals basis (TB-LMTO). Using this we have studied the effect of short-range ordering and clustering on the density of states, optical conductivity and reflectivity of 50-50 CuZn alloys. Our results are in good agreement with alternative techniques. We argue that the TB-LMTO-GASR is a feasible, efficient and quantitatively accurate computational technique for the study of environmental effects in disordered binary alloys.

PACS numbers: 61.46.+w, 36.40.Cg, 75.50.Pp

I. INTRODUCTION

Binary alloys involving equal proportions of a noble metal Cu and a divalent metal Zn have a stable low temperature β -phase which sits immediately to the right of the pure face-centered cubic Cu phase in the alloy phase diagram [1, 2]. This phase, called β brass, has a body-centered cubic structure. At high temperatures the alloy forms a disordered body-centered cubic structure. At around 730K it orders into the B2 structure with two atoms per unit cell. The alloy satisfies the Hume-Rothery rules [3] and has the same ratio of valence electrons to atoms. Jona and Marcus [1] have shown from a density functional theory (DFT) based approach that within the local density approximation (LDA), it is the body-centered based B2 which is the stable ground state. They also showed that if we include the gradient corrections (GGA) then we get a tetragonal ground state lower in energy by 0.1 mRy/atom. This is in contradiction with the latest experimental data. The alloying of face-centered cubic Cu with an equal amount of Zn leads to a body-centered stable phase. Zn has only one more electron than Cu. This is an interesting phenomenon. CuZn alloys also have anomalously high elastic anisotropy. This makes the theoretical study of CuZn an interesting exercise for a proposed theoretical technique.

One of the earliest first-principles density functional based study of the electronic properties of CuZn was by Bansil [4]. The authors had studied the complex bands of α -phase of CuZn using the Korringa-Kohn-Rostocker (KKR) method coupled with the coherent potential approximation (CPA) to take care of disorder. They com-

mented on the effects of charge transfer and lattice constants on the electronic structure. They found the electronic distribution of this alloy to be of a split band kind with the centers of the Cu and Zn d -bands well separated from each other. Their Zn d -bands showed hardly any dispersion and were shown only schematically in their figures. In a later work Rowlands [5] generalized the CPA to a non-local version (NL-CPA) and studied the effects of short-range ordering in CuZn. Their technique was based on an idea of renormalization in reciprocal space suggested by Jarrell and Krishnamurthy [6].

The order-disorder transition in CuZn is a classical example of a true second order transition. Several very early investigations on this alloy have been reviewed by Nix and Shockley [7] and Guttman [8]. These investigations, of course, were rather crude, since sophisticated approaches to deal with disordered alloys had really not been developed at that time. However, it was recognized that a knowledge of the short-range order correlations above the critical temperature should be of considerable interest. Early neutron scattering experiments were carried out on β -brass by Walker and Keating [9]. The Warren-Cowley short-range order parameter, defined by $\alpha(R) = 1 - P_{AB}(R)/x$, where x was the concentration of A and $P_{AB}(R)$ was the probability of finding an A atom at a distance of R from a B atom, was directly obtained from the diffuse scattering cross-section :

$$\frac{d\sigma}{d\Omega} = x(1-x)(b_A - b_B)^2 \sum_R \alpha(R) f(K) \exp(iK \cdot R)$$

b_A, b_B were the scattering lengths of A and B atoms, and $f(K) = \exp(-C|K|^2)$ was the attenuation factor arising from thermal vibrations and static strains. The experimental data for the short-range order parameter as a function of temperature are thus available to us. A Ising-like model using pair interactions was studied by Walker

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and Chipman [10] and the short-range order was theoretically obtained. However, the pair interactions were simply fitted to the experimental values of the transition temperature T_C and in that sense it was an empirical theory. The experimental estimate of the nearest neighbour Warren-Cowley parameter was found to be varying between -0.171 to -0.182 at around 750K.

In a later work using the much more sophisticated *locally self-consistent Green function* (LSGF) approach based on the tight-binding linear muffin-tin orbital (TB-LMTO) technique Abrikosov *et.al.* [11] studied CuZn alloys. The authors argued that earlier studies of the mixing enthalpies of CuZn using the standard coherent potential approximation approaches [12]-[16] showed significant discrepancies with experiment. The discrepancies were assumed to partly arise from the neglect of charge transfer effects and partly because of short ranged ordering (SRO). The main thrust of this technique, which was based on an earlier idea of a locally self-consistent multiple scattering (LSMS) by Wang *et.al.* [17], was to go beyond the CPA and include the effects of the immediate environment of an atom in the solid. The LSMS gave an excellent theoretical estimate of the ordering energy in CuZn : 3.37 mRy/atom as compared to the experimental value of 3.5 mRy/atom. The LSGF approach correctly predicted ordering tendency in CuZn on lowering temperature and combining with a Cluster Variation-Connolly Williams (CVM-CW) obtained a value of the nearest neighbour Warren-Cowley SRO parameter $\alpha = -0.15$. Subsequently Bruno *et.al.* [18] proposed a modification of the CPA including the local field effects and showed that charge transfer effects can be taken into account as accurately as the O(N) methods just described. They applied their approach to the CuZn alloys.

One of the earlier works on the optical property of CuZn alloy was the determination of the temperature variation of optical reflectivity by Muldower [19]. The author attempted to explain the color of the disordered β -brass CuZn alloy via the internal photoelectric effect [20]. Although, the experimental data also contained the contribution from plasma oscillations, the author claimed that the optical reflectivity helps to explain the band picture of the alloys as a function of the inter-atomic spacing. In order to explain the optical properties, Amar *et.al.* [21]-[23] studied the band structure of CuZn using the KKR method. However, they had used the virtual crystal approximation, replacing the random potential seen by the electrons by an averaged one. This is now known to be particularly inaccurate for split band alloys.

The above discussion was necessary to bring into focus the following points : in the study of alloys like CuZn it would be interesting to address the effects of charge transfer and short-range ordering. In this communication we shall address exactly these two points. We shall propose the use of the augmented space recur-

sion (ASR) coupled with the tight-binding linear muffin-tin orbitals basis (TB-LMTO) [24] to study the effects of short-range ordering on both the electronic structure and the optical properties of β -CuZn alloy at 50-50 composition. We should like to stress here that the TB-LMTO-ASR addresses precisely these effects with accuracy : the density functional self-consistent TB-LMTO takes care of the charge transfer, while the local environmental effects which are essential for the description of SRO are dealt with by the ASR. The TB-LMTO-ASR and its advantages has been extensively discussed earlier in a review by Mookerjee [25] and in a series of articles [24, 26, 27, 28, 29, 30]. We would like to refer the interested readers to these for details.

II. SPECTRAL FUNCTIONS, COMPLEX BANDS AND DENSITY OF STATES FOR 50-50 CUZN

In this section we shall introduce the salient features of the ASR which will be required by us in our subsequent discussions.

We shall start from a first principle TB-LMTO set of orbitals [31, 32] in the most-localized representation. This is necessary, because the subsequent recursion requires a sparse representation of the Hamiltonian. The TB-LMTO second order tight-binding Hamiltonian $\mathbf{H}^{(2)}$ is described by a set of *potential parameters* : \mathbf{C}_R , $\mathbf{E}_{\nu R}$, Δ_R and \mathbf{o}_R which are characteristic of the atoms which sit on the lattice sites labelled by R , and a structure matrix $\mathbf{S}_{RR'}$ which is characteristic of the lattice on which the atoms sit. For a substitutionally disordered alloy, the structure matrix is not random but the potential parameters are and can be described by a set of random *occupation variables* $\{n_R\}$. We may write :

$$C_{RL} = C_L^A n_R + C_L^B (1 - n_R)$$

and similar expressions for the other potential parameters. The random site-occupation variables $\{n_R\}$ take values 1 and 0 depending upon whether the muffin-tin labelled by R is occupied by A or B -type of atom. The atom sitting at $\{R\}$ can either be of type A ($n_R = 1$) with probability x or B ($n_R = 0$) with probability y .

In the absence of short-range order, the augmented space formalism associates with each random variable n_R an operator \mathbf{M}_R whose spectral density is its probability density.

$$p(n_R) = -\frac{1}{\pi} \lim_{\delta \rightarrow 0} \text{Im} \langle \uparrow_R | ((n_R + i\delta)\mathbf{I} - \mathbf{M}_R)^{-1} | \uparrow_R \rangle$$

The operator \mathbf{M}_R acts on the “configuration space” of the variable n_R , Φ_R spanned by the configuration states $|\uparrow_R\rangle$ and $|\downarrow_R\rangle$. The augmented space theorem [26] states

that a configuration average can be expressed as a matrix element in the “configuration space” of the disordered system :

$$\ll A(\{n_R\}) \gg = \langle \{\emptyset\} | \tilde{\mathbf{A}}(\{\mathbf{M}_R\}) | \{\emptyset\} \rangle \quad (1)$$

where,

$$\tilde{\mathbf{A}}(\{\tilde{\mathbf{M}}_R\}) = \int \dots \int A(\{\lambda_R\}) \prod d\mathbf{P}(\lambda_R).$$

$\mathbf{P}(\lambda_R)$ is the spectral density of the self-adjoint operator $\tilde{\mathbf{M}}_R$, and the configuration state $|\{\emptyset\}\rangle$ is $\prod_R^\otimes |\uparrow_R\rangle$. Applying (1) to the Green function we get :

$$\ll \mathbf{G}(\mathbf{k}, z) \gg = \langle \mathbf{k} \otimes \{\emptyset\} | (z\tilde{\mathbf{I}} - \tilde{\mathbf{H}}^{(2)})^{-1} | \mathbf{k} \otimes \{\emptyset\} \rangle. \quad (2)$$

where \mathbf{G} and $\mathbf{H}^{(2)}$ are operators which are matrices in angular momentum space, and the augmented \mathbf{k} -space basis $|\mathbf{k}, L \otimes \{\emptyset\}\rangle$ has the form

$$(1/\sqrt{N}) \sum_R \exp(-i\mathbf{k} \cdot \mathbf{R}) |R, L \otimes \{\emptyset\}\rangle.$$

The augmented space Hamiltonian $\tilde{\mathbf{H}}^{(2)}$ is constructed from the TB-LMTO Hamiltonian $\mathbf{H}^{(2)}$ by replacing each

random variable n_R by the operators $\tilde{\mathbf{M}}_R$. It is an operator in the augmented space $\Psi = \mathcal{H} \otimes \prod_R^\otimes \Phi_R$. The ASF maps a disordered Hamiltonian described in a Hilbert space \mathcal{H} onto an ordered Hamiltonian in an enlarged space Ψ , where the space Ψ is constructed as the outer product of the space \mathcal{H} and configuration space Φ of the random variables of the disordered Hamiltonian. The configuration space Φ is of rank 2^N if there are N muffin-tin spheres in the system. Another way of looking at $\tilde{\mathbf{H}}^{(2)}$ is to note that it is the *collection* of all possible Hamiltonians for all possible configurations of the system.

This equation is now exactly in the form in which recursion method may be applied. At this point we note that the above expression for the averaged $G_{LL}(\mathbf{k}, z)$ is *exact*. The recursion method addresses inversions of infinite matrices of the type associated with the Green function [33]. Once a sparse representation of an operator in Hilbert space, $\tilde{\mathbf{H}}^{(2)}$, is known in a countable basis, the recursion method obtains an alternative basis in which the operator becomes tridiagonal. This basis and the representations of the operator in it are found recursively through a three-term recurrence relation. The spectral function is then obtained from the continued fraction :

$$\ll G_{LL}(\mathbf{k}, z) \gg = \frac{\beta_{1L}^2}{z - \alpha_{1L}(\mathbf{k}) - \frac{\beta_{2L}^2(\mathbf{k})}{z - \alpha_{2L}(\mathbf{k}) - \frac{\beta_{3L}^2(\mathbf{k})}{\ddots}}} = \frac{\beta_{1L}^2}{z - E_L(\mathbf{k}) - \Sigma_L(\mathbf{k}, z)} \quad (3)$$

where $\Gamma_L(\mathbf{k}, z)$ is the asymptotic part of the continued fraction. The approximation involved has to do with the termination of this continued fraction. The coefficients are calculated exactly up to a finite number of steps $\{\alpha_n, \beta_n\}$ for $n < N$ and the asymptotic part of the continued fraction is obtained from the initial set of coefficients using the idea of Beer and Pettifor terminator [34]. Haydock and coworkers [35] have carried out extensive studies of the errors involved and precise estimates are available in the literature. Haydock [36] has shown that if we carry out recursion exactly up to N steps, the resulting continued fraction maintains the first $2N$ moments of the exact result.

The self-energy $\Sigma_L(\mathbf{k}, z)$ arises because of scattering by the random potential fluctuations.

The average spectral function $\ll A_{\mathbf{k}}(E) \gg$ is related to the averaged Green function in reciprocal space as :

$$\ll A_{\mathbf{k}}(E) \gg = \sum_L \ll A_{\mathbf{k}L}(E) \gg,$$

where

$$\ll A_{\mathbf{k}L}(E) \gg = -\frac{1}{\pi} \lim_{\delta \rightarrow 0^+} \{\text{Im} \ll G_{LL}(\mathbf{k}, E - i\delta) \gg\}.$$

To obtain the complex bands for the alloy we fix a value

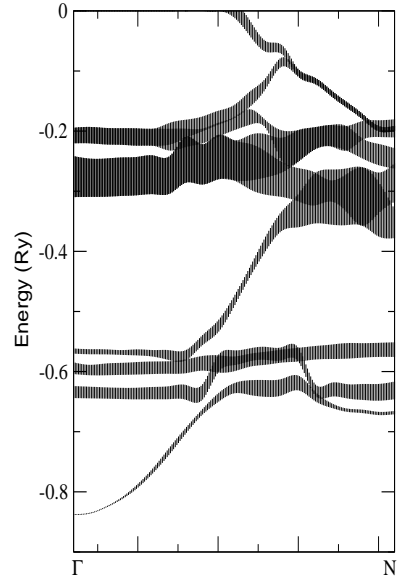
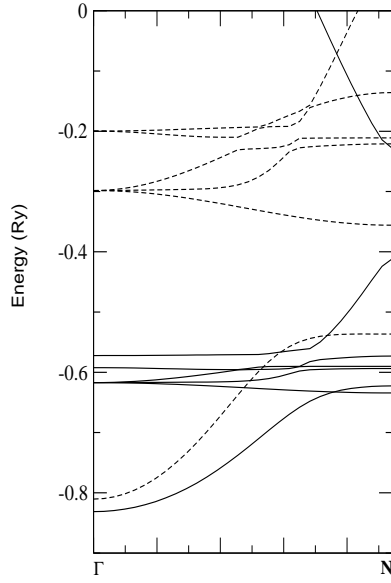


FIG. 1: (left) Bands for pure Cu and Zn in bcc lattices with the dashed lines are for Cu and the full lines for Zn. (right) Complex bands

for \mathbf{k} and solve for :

$$z - E_L(\mathbf{k}) - \Sigma_L(\mathbf{k}, E) = 0.$$

The real part of the roots will give the position of the bands, while the imaginary part of roots will be proportional to the disorder induced broadening. Since the alloy is random, the bands always have finite lifetimes and are fuzzy.

We have used this reciprocal space ASR to obtain the complex bands and spectral functions for the CuZn al-

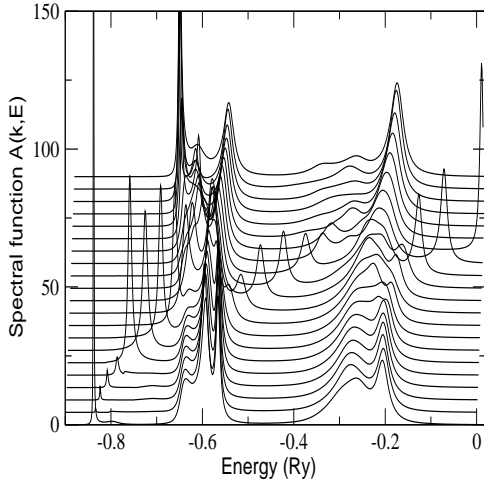


FIG. 2: Spectral functions for the CuZn alloy for \mathbf{k} -vectors along the Γ to N direction in the Brillouin zone.

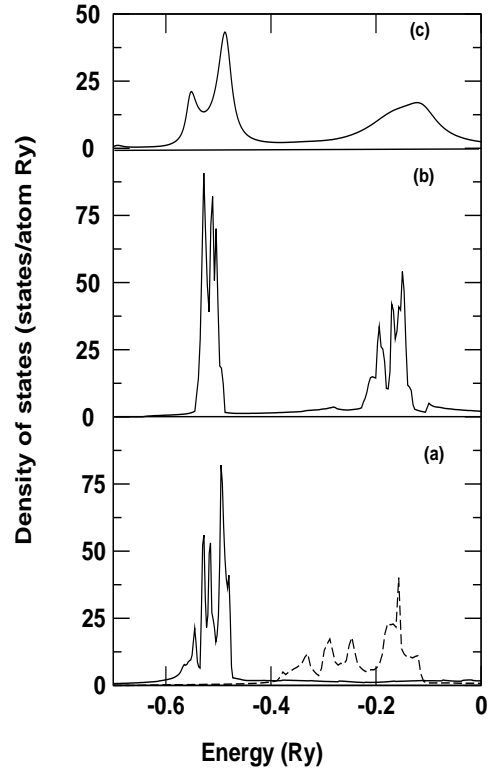


FIG. 3: (bottom) Density of states of pure Zn (solid lines) and Cu (dashed lines) in the same bcc lattice as the 50-50 CuZn alloy. (centre) Density of states for ordered B2 50-50 CuZn alloy. (top) Density of states for the disordered bcc 50-50 CuZn alloy. These results are comparable to the single-site CPA.